

# AN ISOTOPE EFFECT IN THE COLLECTION ON CHARGED PLATES OF ( $n, \gamma$ ) RECOIL PRODUCTS OF BROMINE

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**ABSTRACT.** A study of the relative yields of  $\text{Br}^{80}$ ,  $\text{Br}^{80m}$  and  $\text{Br}^{82}$  following an irradiation of  $\text{C}_6\text{H}_5\text{Br}$  for a duration of 9 days, by an analysis of the time-decay curves, show that the apparent yield of  $\text{Br}^{80}$  on the anode plate is roughly twice that of  $\text{Br}^{82}$ . These results are discussed, *vis-a-vis*, standard data for the thermal neutron capture cross sections of corresponding target atoms,  $\text{Br}^{79}$  and  $\text{Br}^{81}$  and their relative abundances. These findings, considered along with the probable counting efficiency for the resulting radioactive products and their decay characteristics, point to the existence of a small but definite net isotope effect in the overall process of (i) recoil, (ii) charge acquisition and (iii) collection on the charged plate.

## INTRODUCTION

Results of early workers (Fermi *et al.*, 1935; Libby and Vault, 1939, 1941 and Goldsmith and Bluerer, 1950) on the use of charged plates for collecting the ( $n, \gamma$ ) recoil products show marked differences in respect of relative yields collecting on the plates of either sign and of a separation or otherwise of isotopic and isomeric products. Fermi *et al.* (1935) found in the case of methyl or ethyl iodide vapour under neutron irradiation, the polarity of the collecting electrode was not significant. Similarly Libby and de Vault (1939 & 1941) find equal enrichment of  $\text{Br}^{80}$  isomers on the anode and cathode. On the contrary, the results of Paneth and Fay (1935 and 1936) on the separation of radioisotopes of As as well as of bromine and iodine forming under the Szilard-Chalmers' process showed a marked dependence of the yield not only on the sign of the electrode but on its chemical nature and physical condition of the surface. With Pt electrodes, for instance, no activity collects in the case of irradiation of aliphatic halogen compounds, while with smooth Ag or Cu electrodes the active products are deposited exclusively on the anode. In the case of bromobenzene, however, products collect on both anode and cathode in the ratio of roughly 2:1. The results of Capron (1946) are at further variance, more activity collects on the cathode than on the anode in the case of  $\text{C}_2\text{H}_4\text{Br}_2$ , while it is the reverse in the case of  $\text{C}_6\text{H}_5\text{Br}$ . This last finding of preferential collection on the anode appears to be of more frequent occurrence as, for instance, also in the separation of  $\text{In}^{114}$  isomers (Goldsmith and Bluerer, 1950).

There is a similar lack of agreement in respect of whether or not an isotopic and isomeric enrichment occurs in the products of the recoil process collecting on the charged plates. Fox and Libby (1952) Roul and Libby (1953) and Chien and Willard (1954) find no isotopic effect in the retention (fraction of active products left in the original organic medium unrecovered) in the case of *iso*- and *n*-propyl bromide, while Shaw (1951 and 1956) as well as Capron and co-workers (1946, 1952 and 1953) find important isotopic and even isomeric effects at least in the case of aromatic bromo-compounds. No agreed mechanism is available for the secondary reactions following the  $(n, \gamma)$  recoil reaction, to account for the relative yields on the charged plates of the different isotopic and isomeric products as in the case of bromobenzene. The following work has been undertaken with the object of obtaining experimental data under controlled conditions which would help in understanding the role of ionization in the above, an aspect relatively less studied hitherto. The present paper reports results for the collection on charged plates of radioisotopes of bromine in a state of high specific activity and of the associated isotope effect.

#### EXPERIMENTAL

About 500 ml of bromobenzene were irradiated in a pyrex beaker by a 50mC source of (Ra+Be) plunged in the liquid. The neutron source was surrounded by 2 cm of paraffin and a thin walled glass tube. This glass sheath was necessary as both paraffin and polythene were found to be acted upon by bromobenzene under the action of the accompanying high energy gamma radiation. The

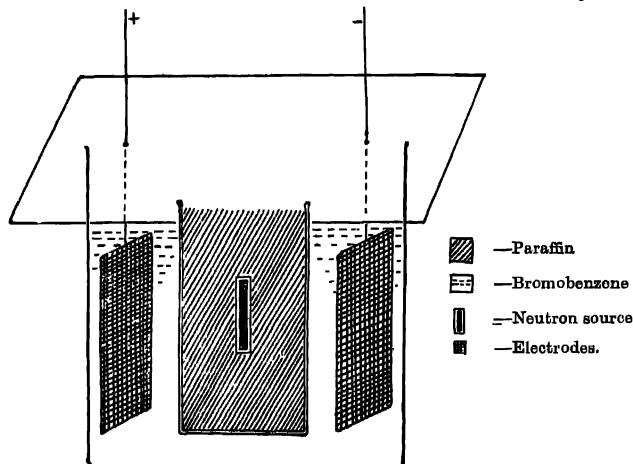


Fig. 1. Arrangement for the collection of  $(n, \gamma)$  recoil products of bromine on charged plates.

electrodes consisting of two parallel plates of either (1) copper with a thin coat of agar-agar gel containing 0.1% of NaOH or (2) silver with or without a trace of AgBr, were placed 6 cms apart and symmetrically with respect to the neutron source, as shown in Fig. I. The field was provided by a battery of 90 volts connected across the electrodes. Irradiations were conducted for a period of 9 days corresponding to about six-times the half-life of the longest lived isotope, viz. 36 hr Br-82. Sometimes a field of 1050 volts was applied during the last 5 hours of irradiation. The radio-isotopes were recovered in the end from the two charged plates separately as follows. In the case of the gel-coated copper electrodes, the gel was melted by warming and the liquid collected was evaporated directly in a counting tray and in the case of the Ag electrodes, the isotopes were recovered by washing the surface with a small amount of ammonia and evaporating the liquid to dryness in a counting tray. Separated in this way, the product was in a state of high specific activity, the amount of inactive bromine being negligible.

## RESULTS

The activities collected on the positive and negative electrodes were measured separately with a thin end-window G. M. counter under conditions of constant geometry. From an analysis of the corresponding time-decay curves the relative yields of different radioisotopes present in the fraction collected were computed. From two measures of the total activity produced in the liquid, with and without the electric field, determined with a liquid counter, the percentage retention was calculated. This varied between 60 to 70% for all the isotopes considered together. Decay curves (Figs. 2 and 3) which are typical of numerous observations show that three activities Br-82 (36 hr) and the metastable Br-80 $m$  (4.4hr) and her ground state Br-80 (18 min) are produced. Also some of the last activities were directly formed from the target Br-79.

The use of extremely thin end-window counter permitted the counting of 80 KcV gammas, of which about 45% are internally converted, with an efficiency comparable to the counting of the betas from Br-80 and Br-82. Countings with a scintillation counter with and without filters for the betas justified this.

The relative yields given in Table I of the different activities collecting on the two electrodes are typical of a series of experiments.

TABLE I

| Activity | Anodo | Cathodo |
|----------|-------|---------|
| Total    | 450   | 220     |
| 36-hour  | 115   | 88      |
| 18-min   | 200   | 100     |
| 4.4-hour | 135   | 32      |

The periods of the two isomers are such that they reach transient equilibrium during the duration of the experiment and the shorter lived (18 min) Br-80 decays with the same period, *viz.*, 4.4 hours as its parent Br-80m. Hence of the total 4.4. hour activity measured one half is due to the daughter product.

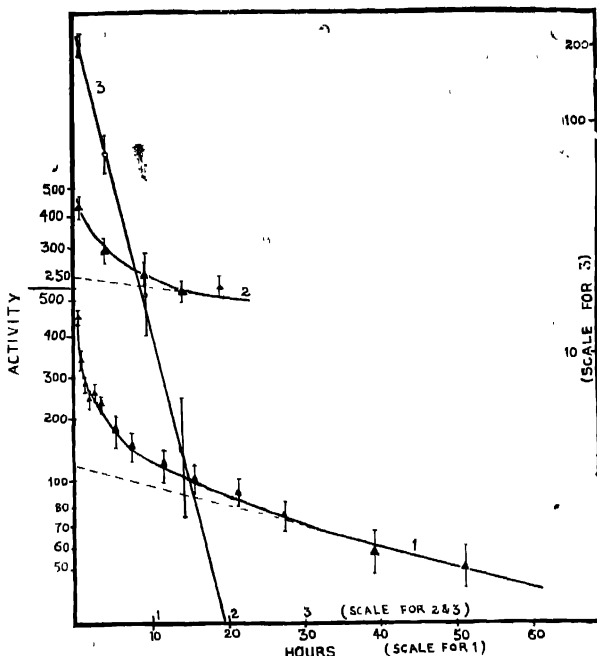


Fig. 2. Analysis of the decay curves of the activity collecting on the anode.

Positive Plate 1. Decay curve - Br-80, Br-80m, Br-82, 2. Decay curve : Br-80 & Br-80m, 3. Half-life line - Br-80.

This 'half' value together with the 18 min. activity directly formed from the target represents the total Br-80 collected. Table II shows the net values of the different radiostopes directly formed from the target.

TABLE II

| Isotope  | Anode | Cathode |
|----------|-------|---------|
| Br-82    | 115   | 88      |
| Br-80    | 200   | 100     |
| Br-80 m. | 68    | 16      |

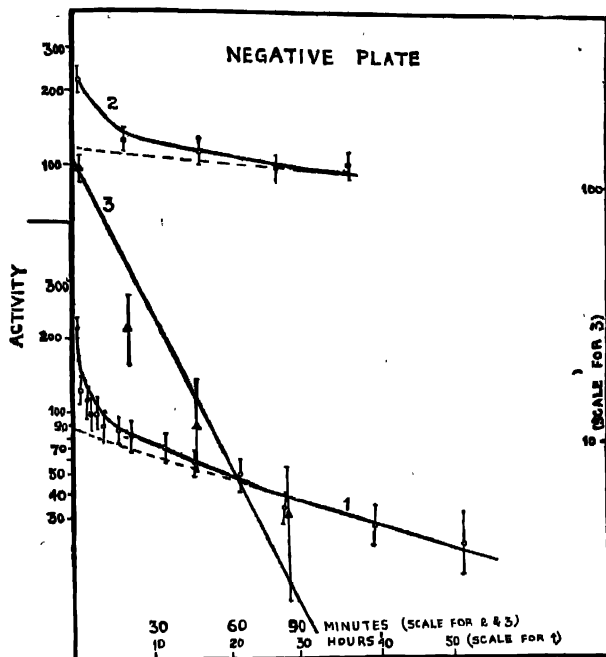


Fig. 3. Analysis of the decay curve of the activity collecting on the anode.

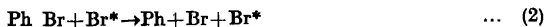
1. Decay curve: Br-80, Br-80<sub>m</sub> & Br-82, 2. Decay curve: Br-80 & Br-80<sub>m</sub>,  
3. Half-life line: Br-80.

#### DISCUSSION

In the formation of Br-80 by the  $(n, \gamma)$  reaction the maximum energy of the gamma emitted is 7.88 MeV (Groshev *et al.*, 1959) which gives 416 eV as the corresponding maximum recoil energy of the Br-80 nucleus, which is adequate for its rupture from the parent molecule. The initial recoil-rupture reaction



is, according to Libby (1947), followed by



As a recombination of these high energy particles may not be readily possible, Shaw (1956) suggests the following secondary reactions:



Reactions (3) and (4) tend to increase the Szilard-Chalmers' extraction yield while the isotope exchange reaction Eq.(5).



leads to increased retention. This is the basis of concentrating radioisotopes by the Szilard-Chalmer technique.

In the above mechanism, it is to be noted, that ionization is not referred to as a necessary stage. As against this, the results presented above as well as those reported earlier by Capron *et al* (1958) point to the appearance of ionization at some stage in the process. In our experiment, both positively and negatively charged particles have been collected (*vide* Table II). With a high factor of internal conversion ( $\sim 45\%$ ) associated with the transition Br-80 $\rightarrow$ Br 80m, a fraction of the initially formed Br-80 is to be expected to be in the Br $^+$  state, following considerable electron loss due to Auger effect. This accumulation of charge, Goldsmith and Bluerer (1950) have shown, may lead to molecular dissociation. Earlier, Cooper (1942) had worked out the theoretical basis for the occurrence of such molecular dissociations occurring as a consequence of the Franck-Condon principle.

These considerations account for the positively charged particles collecting on the cathode and of the concentration of the ground state isomer Br-80 on the cathode. The extreme instability of the Br $^+$ , however, leads to a greater fraction of it to be changed to Br $^-$  finally during transit through the bromobenzene medium. A value of 5.4 for the dielectric constant of the medium is considered high enough to bring about this conversion. These results finally lead to a greater yield on the anode than on the cathode as observed. It is clear that other modes of ionization have to be contemplated, in addition to the Auger consequence following internal conversion, for explaining the collection on charged plates of the metastable isomer and, more specially the isotope Br-82 which does not undergo isomeric transition.

The other observation of interest is the occurrence of an isotope effect in the relative yields of the radio-isotopes Br-80, Br-80 m and Br-82 collecting on either electrode. The relative yield ( $\gamma$ ) for a given species is directly related to the capture cross-section ( $\sigma$ ) of the corresponding target nucleus and its amount ( $n$ ) in the path of the neutron beam. We may thus write for the yield,

$$\gamma_i = \theta_i \sigma_i n_i$$

Here  $\theta$  is the fraction of the given product finally collecting on a given charged plate. In the absence of an isotope effect this fraction ( $\gamma/\sigma n$ ) should be the same for all the species. Table III shows the relative yields together with known data for the percentage natural abundance ( $n$ ) and the capture cross-section ( $\sigma$ ) of the corresponding target nuclei Br-79 and Br-81.

TABLE III

| Target data         |         | Product yields |                   |          |                   |
|---------------------|---------|----------------|-------------------|----------|-------------------|
|                     |         | Anode          |                   | Cathode  |                   |
| $\sigma$ (barns)    | $n(\%)$ | $\gamma$       | $\gamma/\sigma n$ | $\gamma$ | $\gamma/\sigma n$ |
| Br-79 (18 min.) 8.5 | 50.5    | 200            | 0.466             | 100      | 0.233             |
| Br-79 (4.4 hr.) 2.9 | 50.5    | 68             | 0.466             | 16       | 0.109             |
| Br-81 3.5           | 49.5    | 115            | 0.665             | 88       | 0.507             |

Results for the positive plate show the occurrence of a marked isotope effect in the formation and the collection of the isotopes, Br 80 and Br 82 in contrast with its absence as between the two isomers Br-80 *m* and Br-80 as shown by the characteristic ( $\gamma/\sigma n$ ) values. In the case of the negative plate however, an additional enrichment of the isomers is also apparent. This undoubtedly arises from the predominance of Br<sup>+</sup> in the ground state of Br-80 following the internal conversion—ionization mechanism discussed above. The value for ( $\gamma/\sigma n$ ) for Br-80 is over twice that for Br-80 *m* on the negative plate, while the two values are the same for positive plate.

The earlier results of Shaw (1956) indicate a similar order of retention as between the two isomers. Our results however differ from those of Shaw in respect of the order of the yield as between the lighter and heavier isotopes. The formation of active water-soluble compounds, other than HBr and elementary bromine, during accompanying radiolysis is considered one of the causes for the variable yields reported by earlier workers, employing aqueous extraction to concentrate the recoil products. It would thus appear that the method adopted in the present work of collecting the products on dry charged plates would minimize these variables. A more detailed investigation in respect of the influence of field intensity, nature of the target substance and possibly temperature, would be helpful in understanding some of the secondary reactions following the ( $n, \gamma$ ) reaction.

## REFERENCES

- Capron, 1946, *Nature*, **157**, 806.  
 Capron and Oshima, 1952, *J. Chem. Phys.*, **20**, 1403.  
 Capron and Crevecoeur, 1952, *J. Chim. phys.*, **49**, 20.  
 Capron and Crevecoeur, 1953, *J. Chem. Phys.*, **21**, 1843.  
 Capron *et al.*, 1958, Proc. Second Int. Conf. (Peaceful Uses of Atomic Energy), Geneva, Sept., 1958.  
 Chien and Willard, 1954, *J. Am. Chem. Soc.*, **76**, 4735.  
 Cooper, 1942, *Phys. Rev.*, **61**, 1.  
 Fay and Paneth, 1935, *Nature*, **135**, 820.  
 Fay and Paneth, 1936, *J. Chem. Soc.*, 384.

- Fermi, Amaldi and others, 1935, *Proc. Roy. Soc.*, A149, 522.  
Fox and Libby, 1952, *J. Chem. Phys.*, 20, 487.  
Groshev, *et al.*, 1959, "Atlas of  $\gamma$ -Ray Spectra for Radiative Capture of Thermal Neutrons" (Pergamon Press, London).  
Goldsmith and Bluerer, 1950, *J. Phy. & Colloid Chem.*, 54, 717.  
Libby and de Vault, 1939, *Phys. Rev.*, 55, 322.  
Libby and de Vault, 1941, *J. Am. Chem. Soc.*, 63, 3216.  
Libby, 1947, *J. Am. Chem. Soc.*, 69, 2623.  
Millman and Shaw, 1956, *J. Chem. Soc.*, 2101.  
Rouland and Libby, 1953, *J. Chem. Phys.*, 21, 1495.  
Shaw, 1951, *J. Chem. Soc.*, 443.  
Shaw and Collie, 1951, *J. Chem. Soc.*, 434.